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HIGH-TEMPERATURE INTEGRAL ABSORPTION IN GLASSES

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The information published in various sources concerning IR absorption of certain glasses is summarized. The results are supplemented by the data of research carried out by the authors. It is proposed to use the integral absorption coefficient calculated for the considered glass compositions in solving the problems of radiation-conductive heat exchange. The resulting data bank will make it possible to predict the integral absorption of glasses containing certain transition elements, primarily, iron.

The contemporary approach to the problem of radiation-conductive heat exchange (RCHE) in glass involves the virtually total rejection of the classical notions based on the solutions of the differential Fourier equation, in which the main

thermophysical parameters of glass were the effective heat conductance and temperature conductivity. With the new approach, the main fundamental optical-thermophysical characteristic is the integral absorption coefficient.

An extensive implementation of the new methods [1] based on solutions of integral-differential equations in practi-

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TABLE 1

Compo- sition	Glass grade	Mass content, %										Note
		SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	SO ₃	Fe ₂ O ₃	Cr ₂ O ₃	Mn ₂ O ₃	
1	Window [2]	75.0	15.6	—	8.8	0.2	—	0.8	0.05	—	—	0.008% FeO
2	Model [2]	75.0	15.6	—	8.8	0.2	—	0.8	0.241	—	—	0.103% FeO
3	The same	75.0	15.6	—	8.8	0.2	—	0.8	0.53	—	—	0.217% FeO
4	"	75.0	15.6	—	8.8	0.2	—	0.8	0.815	—	—	0.284% FeO
5	Container [2]	72.0	14.1	—	6.4	3.7	3.4	0.4	0.45	—	—	—
6	Bottle [2]	70.0	14.6	—	6.4	3.7	5.0	—	0.48	0.096	—	—
7	The same	68.0	14.4	—	6.2	4.0	4.3	0.4	1.4	—	1.11	—
8	Marblite [2]	60.0	15.0	—	6.0	—	0.4	—	0.2	0.4	18.0	—
9	Quartz KI [3]	100.0	—	—	—	—	—	—	—	—	—	—
10	Quartz KV [3]	100.0	—	—	—	—	—	—	—	—	—	0.04% H ₂ O
11	Quartz KSG [3]	100.0	—	—	—	—	—	—	—	—	—	0.02% H ₂ O
12	Model [4]	77.0	16.5	—	6.9	—	—	—	1.0	—	—	Oxidizing conditions
13	The same	77.0	16.5	—	6.9	—	—	—	1.0	0.2	—	Reducing conditions
14	"	77.0	16.5	—	6.9	—	—	—	—	0.2	—	Oxidizing conditions
15	"	77.0	16.5	—	6.9	—	—	—	—	0.2	—	Reducing conditions
16*	"	77.0	16.5	—	6.9	—	—	—	—	—	—	Oxidizing conditions
17**	Window [5]	72.0	14.8	—	9.6	2.5	0.5	0.5	0.13	—	—	—
18	Household [5]	75.0	14.2	0.2	8.3	—	1.6	—	0.046	—	—	—
19	Orange [5]	72.0	15.8	—	9.8	—	0.1	0.4	0.12	—	—	—
20	Chromium [6]	67.0	—	13.5	15.0	—	2.2	1.1	0.33	0.1	—	—
21	Green [6]	68.0	—	15.2	10.2	0.1	2.7	—	2.48	—	0.94	—
22***	X-ray-protective [5]	34.0	2.0	—	—	—	—	—	—	—	—	—
23	Model [7]	70.0	15.0	—	12.0	—	1.0	—	0.2	—	—	Reducing conditions
24	The same	70.0	15.0	—	12.0	—	1.0	—	—	0.1	—	The same

* Composition 16 also contained 0.1% CoO.

** Composition 17 also contained 0.1% TiO₂.

*** Composition 22 also contained 3.0% BaO and 61.0% PbO.

cal calculations of RCHE is significantly obstructed by the absence of reliable published data on integral absorption coefficients for glasses of different chemical compositions and their temperature dependence. Such data are available only for a limited number of glasses. The present study resulted in getting supplementary data on another eight glass compositions.

Integral absorption coefficients can be calculated by integrating the experimentally found spectral characteristics of glasses obtained by high-temperature IR spectroscopy methods. Such studies even now are regarded as “unique”; therefore, the available information is far from exhaustive. However, the data on 24 glass compositions, eight of which (compositions 1 – 8 in Table 1) are results of our studies, can give some reference points for solving this problem.

It should be noted that integration in this case is a rather complicated mathematical problem. The calculations and constructions of plots were performed using software programs. The study used the integral absorption coefficient calculated according to the Rosseland formula:

$$K_R = \frac{\int_0^\infty \frac{dB_{(\lambda,T)}}{dT} d\lambda}{\int_0^\infty \frac{1}{K_{(\lambda,T)}} \frac{dB_{(\lambda,T)}}{dT} d\lambda},$$

where $B_{(\lambda,T)}$ is the Planck function; T is the temperature; λ is the wavelength; $K_{(\lambda,T)}$ is the monochromatic absorption coefficient.

The principal initial data were the spectral and the temperature dependence of the monochromatic absorption coefficient [2 – 7].

In the course of data processing, plots were constructed for all glass compositions in the same scale system, which is convenient for their comparative analysis and processing.

The compositions of the considered glasses are shown in Table 1. The information on the spectral-temperature dependences of the absorption coefficients of these glasses has been accumulated for decades and has been published by five different researchers. Therefore, the selection of compositions of glass was not systematic. Compositions 1 – 8 were investigated by the Department of Chemical Engineering of Ceramics and Glass at the National Technical University of Ukraine (KPI).

The analysis of the compositions established an important positive factor: most of them are within the variation range of the traditional industrial glasses or are sufficiently close to this range. This implies that the composition of what is known as the glass matrix consists of three main oxides (SiO_2 , Na_2O , and CaO) and some others, which we will arbitrarily name the secondary oxides (MgO , Al_2O_3 , and K_2O). This arbitrary distinction is justified in our case, since the latter oxides cannot have a perceptible effect on RCHE.

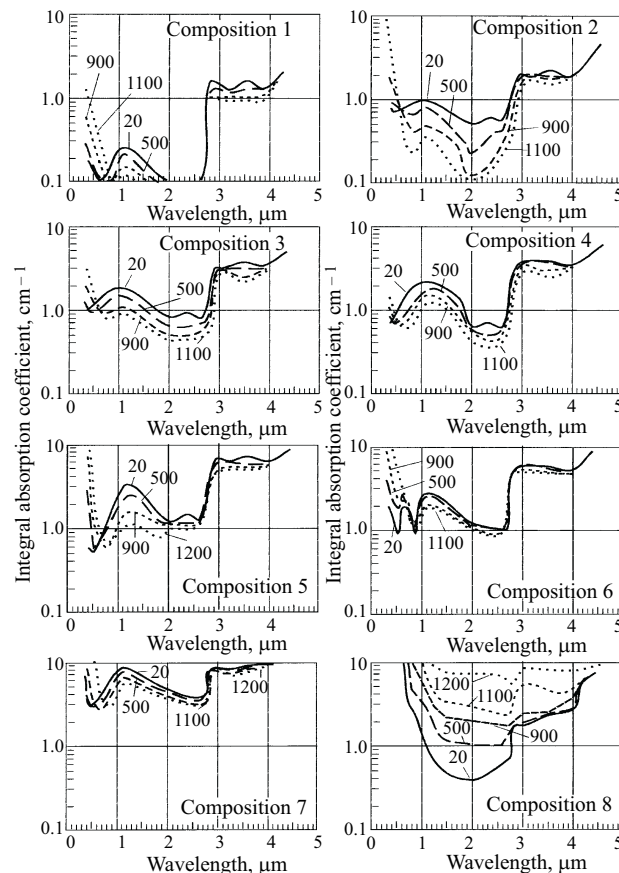


Fig. 1. Spectral characteristics of experimentally studied glasses. Numbers by the curves – temperature (°C).

The following variation ranges were registered for the main components of the glass matrix (%): 60 – 77 SiO_2 , 14 – 16 Na_2O , and 6 – 15 CaO . Only the three quartz glasses (compositions 9 – 11) and the x-ray-protective glass (composition 22) are exceptions from the above.

A more significant spread is registered in the content of the transition element oxides (Fe_2O_3 , Cr_2O_3 , Mn_2O_3 , and CoO). Even with a very slight content of these oxides, the optical characteristics can vary significantly. Unfortunately, in some glasses these oxides are present in combinations, which makes the identification of the role of each of them even more complicated. It is only in our study that a certain strictness can be observed in the variation of Fe_2O_3 content (compositions 1 – 5).

The results of the computer processing of initial data on the temperature dependence of the spectral characteristics of all the glass compositions are presented in Figs. 1 and 2, and the temperature dependence of the integral absorption coefficient of the glasses is shown in Fig. 3.

The most transparent of the considered glasses, namely, the window glass (composition 1) has the minimum integral absorption value. Within the composition series 1 – 4, with an increasing total content of iron oxides, a regular shift of the respective curves upwards along the ordinate axis is ob-

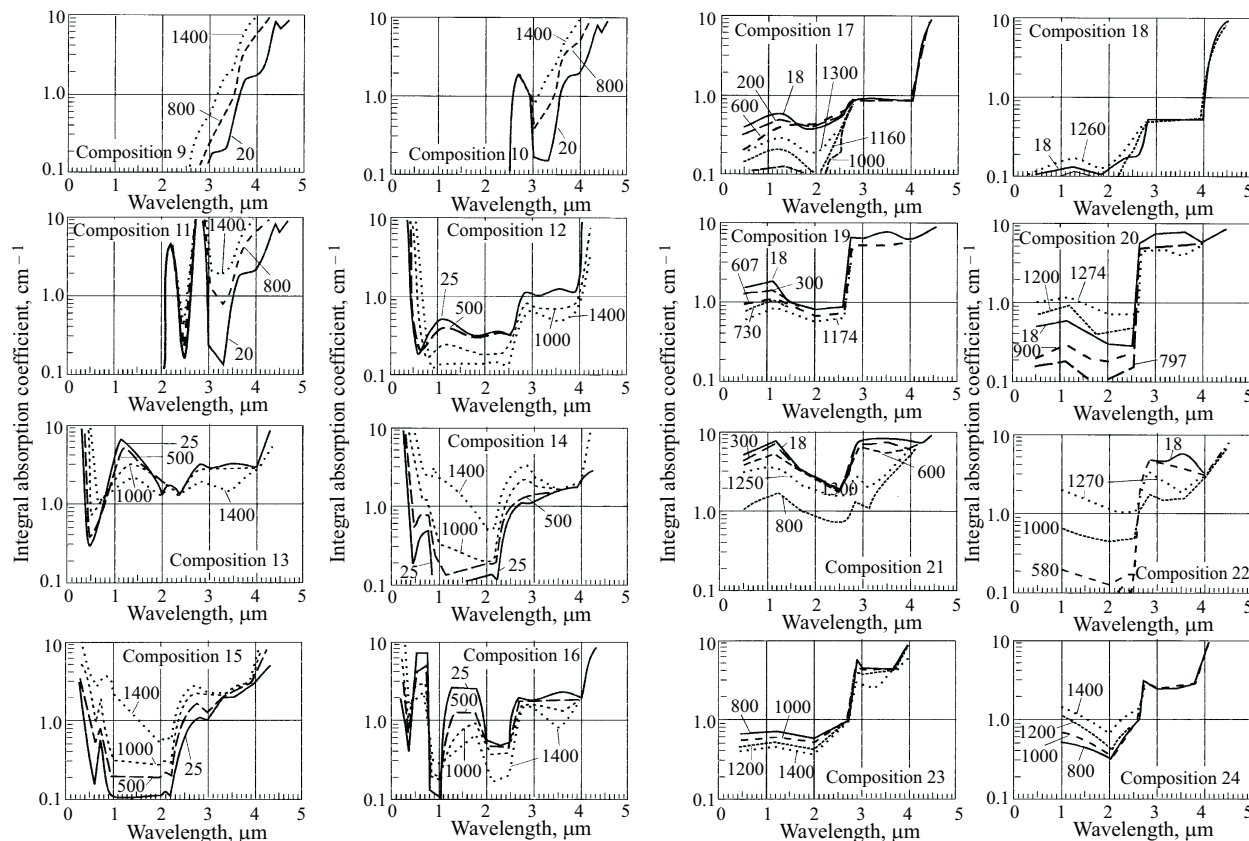


Fig. 2. Spectral characteristics of glasses of various grades found in published sources. Numbers by the curves – temperature (°C).

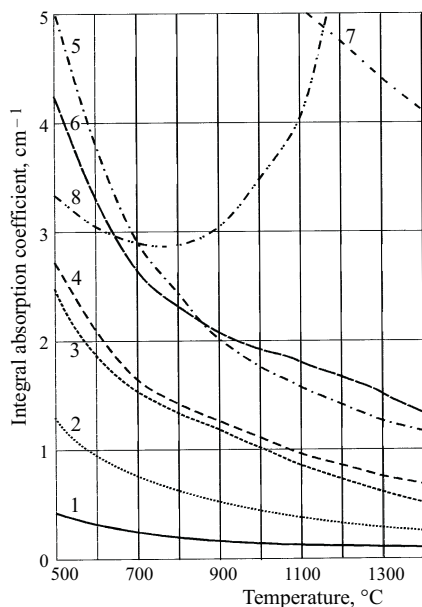


Fig. 3. Temperature dependence of integral absorption coefficient in iron-containing glasses. Curve numbers indicate composition numbers.

served. A certain surprise is caused by the relatively slight change in absorption upon the transition from composition 3 (0.53% Fe_2O_3) to composition 4 (0.815% Fe_2O_3). The

curves are arranged sufficiently close to each other. However, if, instead of regarding the above quoted total content of iron oxides converted to Fe_2O_3 , one considers the part which exists as FeO and accounts for the main absorption band at wavelength 1.1 μm , the observed proximity of the curves can be accounted for. Thus, the regularities of integral absorption variation are traced clearly enough in the series of model glasses 1–4 synthesized in identical conditions. A somewhat unexpected result is seen in the container glass of composition 5. The absorption values weakly correlate with the iron oxides content (this glass was not produced at the University, but was taken for research from a glass factory, and data on the redox conditions of the glass melting were absent).

Glass 6, which in addition to iron oxides (0.48%) also contains chromium oxide (0.096%), in principle has the same level of the integral absorption values as glass 5.

The integral absorption values in glass 7 are very high. This may be the consequence of a substantial content of iron oxides (1.4%).

The glass of composition 8 behaves in a very unexpected way. An abrupt increase in integral absorption is registered starting with temperatures around 800°C, which may be caused by a high content of Mn_2O_3 (18%), as well as a rather high content of Cr_2O_3 (0.4%).

The processing results of the published data are summarized in Fig. 4. Interesting information was obtained for three quartz glasses (compositions 9 – 11). The first glass consists of pure SiO_2 , whereas the second and the third ones contain water (hydroxyl groups $(\text{OH})^-$). The presence of water determines the appearance of some typical absorption bands in the near-IR spectrum, of which the most intense band correlates with the wavelength $2.7 \mu\text{m}$. It is obvious and understandable that the effect of “water” is noticeable most of all at the minimal temperatures. As the temperature increases, this difference gets leveled.

It should be noted that the pure quartz glass KI, as could be expected, has the minimum possible integral absorption values for silicate glasses. The glass KV, containing 0.04% water, has approximately the same shape of the curve as that of the most transparent among the considered glasses: window glass 1 (0.05% Fe_2O_3) and household glass 18 (0.046% Fe_2O_3). In the first of these glasses, the component causing IR absorption is $(\text{OH})^-$ groups, and in the two other glasses, such a component is represented by iron oxides. The glass matrix compositions in the first glass and in the two other glasses are totally different. In this context, one can make a logical conclusion that such glass matrix components as Na_2O , CaO , MgO , and Al_2O_3 do not have a perceptible effect on the integral absorption in glasses.

The studies by Coenen [4] are of interest, as they consider the effect of the melting environment on the spectral characteristics of iron- and chromium-bearing glasses. Glass 12, which contains 1.0% FeO and is melted in highly oxidizing conditions, yields results which well agree with the results we obtained for the glass with the most similar composition (composition 4). Glass 13, containing the same amount of iron but melted in highly reducing conditions, exhibits very high integral absorption values.

The chromium-containing glasses (0.2% Cr_2O_3), melted in highly oxidizing (composition 14) and highly reducing (composition 15) conditions, have a similar curve shape with the clearly expressed minimum at 1000°C . With a further increase in temperature, an increase in the integral absorption is observed. Under reducing conditions, the curve passes slightly above the curve reflecting the oxidizing conditions. However, the effect of the melting medium is not significant. Similar tendencies are observed in the curves for chromium-bearing glasses constructed on the basis of data obtained by other researchers (compositions 20 and 24). The significant increase in the integral absorption in glass 12 observed with increasing temperature now becomes understandable.

Glass 21 is of interest by being a manganese-containing glass. Unfortunately, ferric oxide is present in this glass as well, but the substantial increase in absorption starting with 800°C can be only related to the presence of manganese. This result agrees well enough with our data obtained for glass 8. A totally unexpected result was demonstrated by high-lead x-ray-protective glass (composition 22). Its minimum absorption is registered at the lowest temperature

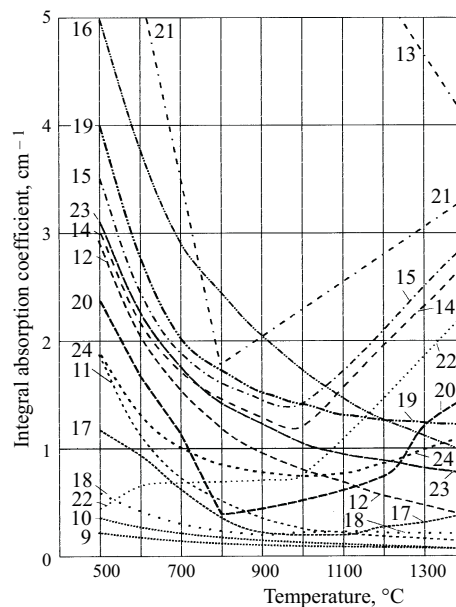


Fig. 4. Temperature dependence of integral absorption coefficient in glasses of various grades found in published sources. Curve numbers indicate composition numbers.

(500°C). As the temperature grows to 1000°C , the absorption virtually does not change, and then starts intensely growing.

Regarding the described series of 24 glasses, the quantitative estimate of the effect of the colorant oxide can be given only for iron-containing glasses. This generalization was based on compositions 1 – 4, 12, 13, 17 – 19, and 23. The selected compositions are the ones in which only iron oxides are present. The results of this correlation are represented in Fig. 5 (the temperatures of 600, 1000, and 1400°C are of the greatest practical significance, since they approximately correlate with annealing, molding, and melting temperatures).

The three curves for oxidizing melting conditions are plotted based on the results obtained for glasses 19 and 13. The absorption values of glass 13 at temperatures of 600 and 1000°C reached beyond the limits of the represented diagram, and yet they were taken into account. The respective points for glass 23 are somewhat below these curves. It is possible that the latter glass had a slightly lower reducing potential.

The curve shapes for oxidizing melting conditions were mainly plotted based on the results obtained for glass 12.

The dots in the curves represented in Fig. 5 indicate the most probable course of the sought dependence for neutral or weakly oxidizing melting conditions. These curves well enough average the obtained values for other considered glasses. They can be recommended as a reference estimate of the integral absorption of iron-containing glasses.

Thus, the present study involved collecting, summarizing, and critical analysis of information regarding the absorption properties of glasses in the visible and near-IR ranges published in the domestic and foreign literature. A theoretic-

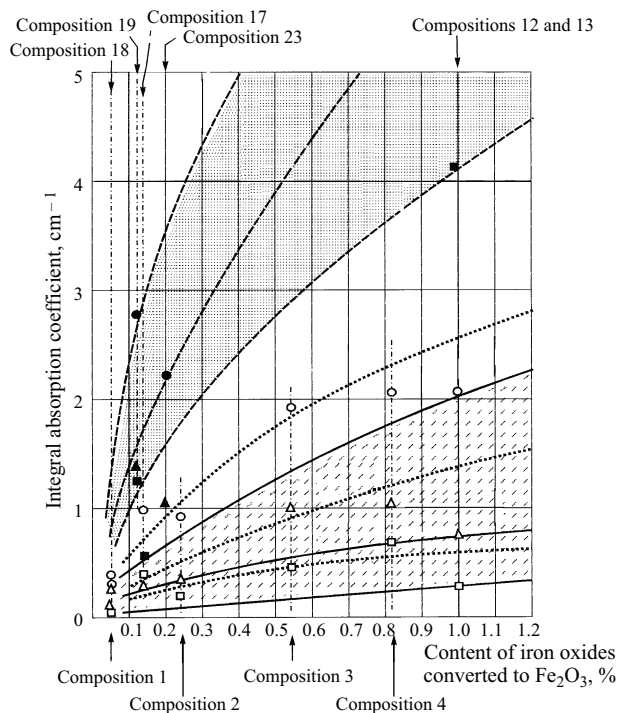


Fig. 5. Integral absorption of iron-bearing glasses: ●, ▲, and ■) 600, 1000, and 1400°C (reducing conditions in melting); ○, △, and □) 600, 1000, and 1400°C (oxidizing conditions in melting).

cal summary analysis is given of the possible effect of certain components which are present in glasses in small quantities but have a strong effect on the absorption capacity.

All known data for 24 glass compositions, 8 of which were experimentally investigated at Kiev Polytechnic Institute, were processed using the developed method and software programs.

A kind of data bank was created, regarding the effect of iron, chromium, cobalt, manganese, and lead oxides on the

integral absorption in glasses within a wide temperature range, as well as for some glass matrix compositions.

A quantitative estimate of the effect of iron oxides (the colorant component most commonly found in industrial glasses) on the integral absorption of glass was made. Since iron can exist in glass in two degrees of oxidation (Fe_2O_3 and FeO), the absorption properties of such glasses significantly depend on the redox potential of the glass in melting, whereas the effect of the melting conditions prevails over the effect of iron oxides. Therefore in the quantitative evaluation of the integral absorption in glasses, one can only use the concept of the confidence value interval. The final diagram makes it possible to give a probabilistic estimate of integral absorption values for iron-containing glasses.

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